

HALLOYSITE NANOTUBES MODIFIED
WITH NANOPARTICLES OF CERIUM OXIDE
FOR HEALTH TECHNOLOGY

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Abstract

Nanoparticles of cerium oxide have been found to possess UV blocking properties, making them a potential replacement for TiO_2 and ZnO in UV-protection formulations. To further enhance their stability and immobility, we synthesized and deposited such nanoparticles on halloysite nanotubes (HNTs) by reacting $\text{Ce}(\text{NO}_3)_3$ and NaOH in aqueous solutions without stabilizers at room temperature. The nanoparticles were < 15 nm. X-ray and electron diffraction analyses confirmed that the cerium dioxide (CeO_2 , ceria) had cubic crystals. With electron microscopy it was shown that the CeO_2 particles were evenly distributed on the HNTs, resulting in low particle agglomeration. The size of the particles correlated linearly with the oxide content in the nanocomposites up to an oxide concentration of 5%. These synthesized nanomaterials were then used to create sunscreens.

Key words: halloysite nanotubes, cerium oxide, nanoparticles, health protection

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Introduction. Solar radiation contains shortwave (UVB, 290–320 nm) and longwave (UVA, 320–400 nm) ultraviolet radiation. Skin inflammation and skin redness are mainly caused by UVB radiation, which is also a major risk factor for cancer [1]. Sunscreen lotions are commonly used and have organic or inorganic UV filters but there are some concerns about their toxicity and ecotoxicity [2, 3]. Inorganic UV filters are based on semiconductors with a suitable band gap, and TiO_2 and ZnO are typically used [4, 5]. The opaqueness of inorganic UV filters can be reduced or eliminated by using nanoparticles [6].

Cerium oxide (CeO_2 , ceria) is a semiconductor, and it has been shown to provide a strong UV barrier. Silicate halloysite nanotubes (HNTs) are parts of a clay material, which is mesoporous [7]. The term mesopores is used to describe pores of dimensions of 2–50 nm. In a study by LIM et al. [8] HNTs were modified by sodium dodecyl sulphate and ZnO to create UV-protective properties in poly(lactic acid)-containing nanocomposites. The obtained nanocomposites exhibited higher UV-blocking properties than composites of poly(lactic acid)@untreated HNTs. In another study, encapsulated HNTs were added to an epoxy system and evaluated before and after 840 h of accelerated weathering. It was shown that the epoxy-coated samples with organic UV stabilizers or lignin had significantly higher UV stability than the epoxy resin without such organic components. It was concluded that the nanoclays loaded with lignin may be used as an UV absorber and increase the weathering performance of epoxy resins [9]. In another study, a textile coating was constructed from a renewable mulukhiyah extract and naturally deposited halloysite nanotubes in the presence of chitosan chains. The UV protection factor was enhanced by 57% compared with the raw textile. The study was presented as a new strategy for the conservation of historical textiles against harmful UV radiation [10]. XU et al. [11] have studied cotton fabrics and used photocatalysts with a UV shielding property based on fluorinated ZnO @halloysite nanotube hybrids. The ZnO @HNTs hybrid particles were prepared by in-situ growth of ZnO nanoparticles on the surface of HNTs with a needle-like microstructure. In the generalizations of the authors, many examples of the use of nanoclay as the carrier of functional ingredients are described [12].

As mentioned, nanoscale CeO_2 might be an alternative to ZnO and TiO_2 with potentially less hazardous properties. In a study, CeO_2 particles were dispersed in a water-reducible polyol polyacrylate dispersion resin, followed by mixing in a polyisocyanate hardener from which films were prepared and exposed to accelerated artificial weathering. The films with CeO_2 nanoparticles were less affected by the UV exposure as compared to the blank polyurethane [13]. JIANG et al. [14] prepared Ce-doped aluminoborate glasses and showed that the materials had significant UV absorption in the UVA, UVB, and UVC (200–290 nm) regions, while still being highly transparent in the visible-wavelength region. The inorganic films were compared to organic-inorganic films that were highly resistant to harsh environments (temperature and pH). Hence, one may argue that inorganic films

may provide UV shields for use in a diverse set of environments, such as greenhouses, vehicle windows, and in various applications in museums. It has also been shown [15] that CeO₂ nanoparticles can be anchored on the surface of HNTs by in situ assembly, and the hybrid architecture of HNTs@CeO₂ brought excellent UV-blocking to the polydimethylsiloxane/HNTs@CeO₂ coating, which is hydrophobic and has a self-cleaning function.

Here, we explore the synthesis of HNTs@CeO₂-based as components in UV protection for the health technology.

Materials and methods. *Synthesis of nanomaterials.* CeO₂/HNTs nanocomposites were obtained by the chemical precipitation of CeO₂ in an alkaline aqueous medium in the presence of HNTs. HNTs@CeO₂ samples with 0.5–5 wt% of CeO₂ were prepared by varying the stoichiometric ratios of the reagents. In an example of the synthesis of the HNTs@CeO₂ samples with 5 wt% CeO₂, 6.25 g of HNTs (NaturalNano, Inc.) was added in 40 mL of distilled water, to which 16.3 mL of a 1 M Ce(NO₃)₃ solution was added. Under stirring, 24.5 mL of a 2 M NaOH solution were added to the resulting suspension until a pH 8–9 was reached. The suspended particles were filtered off, washed until no NO₃[−] could be detected, and dried at 120 °C. (The test for NO₃[−] was carried out by a qualitative reaction with diphenylamine in sulphuric acid.)

Physico-chemical description of nanomaterials. Elemental analysis of materials was carried out by atomic emission spectrometry using an ICPE-9000 instrument, Shimadzu (Table 1). For this analysis, the samples were prepared by microwave decomposition in a mixture of concentrated acid solutions HNO₃:HF (5:1 per volume) using microwave device (XP1500Plus MARS, CEM) for 30 min. The moisture content of the samples was determined using a Moisture Balance MOC-120H, Shimadzu. The samples were heated to 120 °C and kept at a constant temperature for 15 min until a constant mass read out was established.

The crystal structure features of the CeO₂/HNTs nanocomposites were studied by X-ray diffraction (XRD) at standard room conditions using a diffractometer (DRON-4-07) with a wavelength $\lambda = 1.5418 \text{ \AA}$ (CuK α -radiation). Diffraction patterns were recorded in the range of angles $2\theta = 8\text{--}90^\circ$ with a rotation speed of $0.05^\circ \cdot \text{min}^{-1}$. Samples for XRD measurement were prepared by grinding the powders in an agate mortar and subsequent tablet formation.

The materials were characterized using a Transmission Electron Microscope (TEM) (Hitachi H-800) using also the method of electron diffraction in selected areas. Samples for TEM were prepared by dispersing them in a solvent under the influence of ultrasound for up to 5 min and then applying them to a porous carbon substrate. Particles sizes were measured on dark-field images using a linear measurement program with a sampling of more than 40 objects per sample.

Results. *Synthesis and structure of nanomaterials.* The synthesis of the HNTs@CeO₂ nanomaterial was carried out in an aqueous solution without stabilizers at room temperature, which is in line with the principles of “green”

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Results of samples elemental analysis for cerium by atomic emission analysis and water content

Calculated CeO ₂ content, %	CeO ₂ average content, %	The mass sample, mg	Uncertainty, %	H ₂ O content, %
0.5	0.504	192.1	0.022	2.91
		188.5		
		138.6		
1	0.998	182.6	0.011	3.02
		134.6		
		113.4		
2	2.085	170.4	0.109	3.24
		154.9		
		146.3		
3	3.188	201.4	0.02	3.18
		117.3		
		129.6		
4	3.972	162.1	0.051	3.05
		156.0		
		201.4		
5	4.888	203.3	0.062	3.79
		217.4		
		160.9		

chemistry. No organic solvents nor organic particle-growth stabilizers were used. CeO₂ nanoparticles < 15 nm were obtained by the reaction between Ce(NO₃)₃ and NaOH and associated with the HNTs. This approach and synthesis was in line with established methods for the synthesis of CeO₂ nanostructures in aqueous phase [16].

HNTs are often described by the chemical formula Al₂Si₂O₅(OH)₄·nH₂O, where n = 0–2 and it has been established that the thickness of a single wall of a HNT is 10 Å, which corresponds to the silicon-oxygen tetrahedral and aluminohydroxy-oxygen octahedral networks (7.14 Å) and a water monolayer (3 Å). The measured diffractogram of the HNTs (Fig. 1) is consistent with literature data. To identify halloysites, the reflection *d*₀₀₁-value 7.14 Å is used [17]. In the region of 2θ = 18°, the observed signal relates to an aluminum hydroxide impurity. At small angles of the diffractograms, diffraction lines were found that indicate a mixture of tubular halloysite-7Å and tubular halloysite-10Å in the samples. After modification with CeO₂, the line corresponding to the halloysite-10Å disappeared, which was interpreted as an effect of water desorption from the interlayer space of halloysite in HNTs@CeO₂ (5 wt%). On the diffraction patterns of HNTs@CeO₂

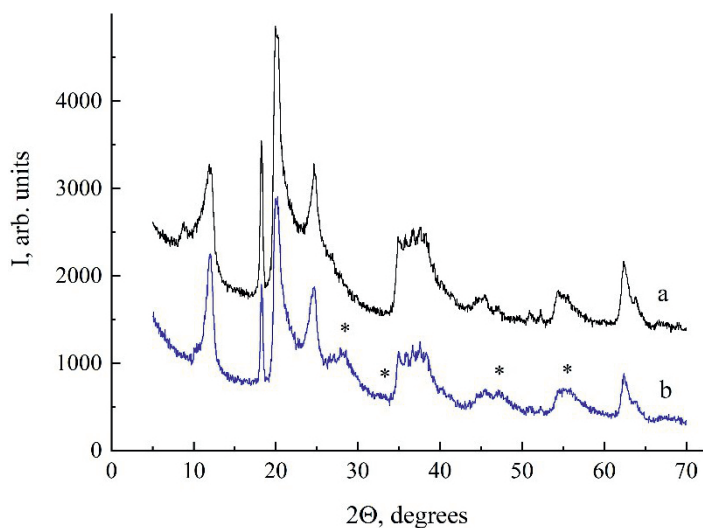


Fig. 1. XRD patterns of the halloysite nanotubes (HNTs) (a) and synthesized HNTs@CeO₂ nanocomposites with 5% (b) the modifier content, * – signals of the cerium oxide

(5 wt%), lines for the cubic fluorite structure of CeO₂ are observed (Fig. 1b), which are consistent with the electron diffraction analysis. The intensity of reflections from the CeO₂ increases with increasing concentration of the modifier (not shown). The large half-width of CeO₂ signals can be interpreted related to the small size of the crystals or low crystallinity. In a general context, it is also of relevance to note the ease of formation of oxygen vacancies in CeO₂ at the nanoscale. These vacancies result in the formation of mixed valence compounds as CeO_{2-x} [18].

Electron microscopic examination of the HNTs@CeO₂ materials..

By analyzing the TEM images we estimated that the particles of HNTs and a typical HNTs@CeO₂ nanocomposite (5 wt% CeO₂) had HNTs particles with a width of approximately 60–90 nm and a length of approximately 450–550 nm. The cerium was evenly distributed on the carrier surface. Hence, we inferred that the CeO₂ nanoparticles were uniformly distributed on the HNTs surfaces. The aggregation of the nanoparticles had been suppressed, and we linked this to the fact that the HNTs particles had prevented direct contact between the CeO₂ particles and, hence, their agglomeration during the preparation of the composites [15].

In the TEM images samples of the HNTs@CeO₂ nanocomposite with two different contents of CeO₂ (3 and 5 wt%), a number of distinctive features can be observed. In the images in Fig. 2a, b, elongated particles of HNTs can be distinguished, on which much smaller spherical particles are deposited, dark in the images in the bright field and light in the dark field. These were the CeO₂ particles. Dark-field TEM images were used to determine the size of the CeO₂ nanoparticles as they have a higher contrast than the HNTs. In the high-magnification image of

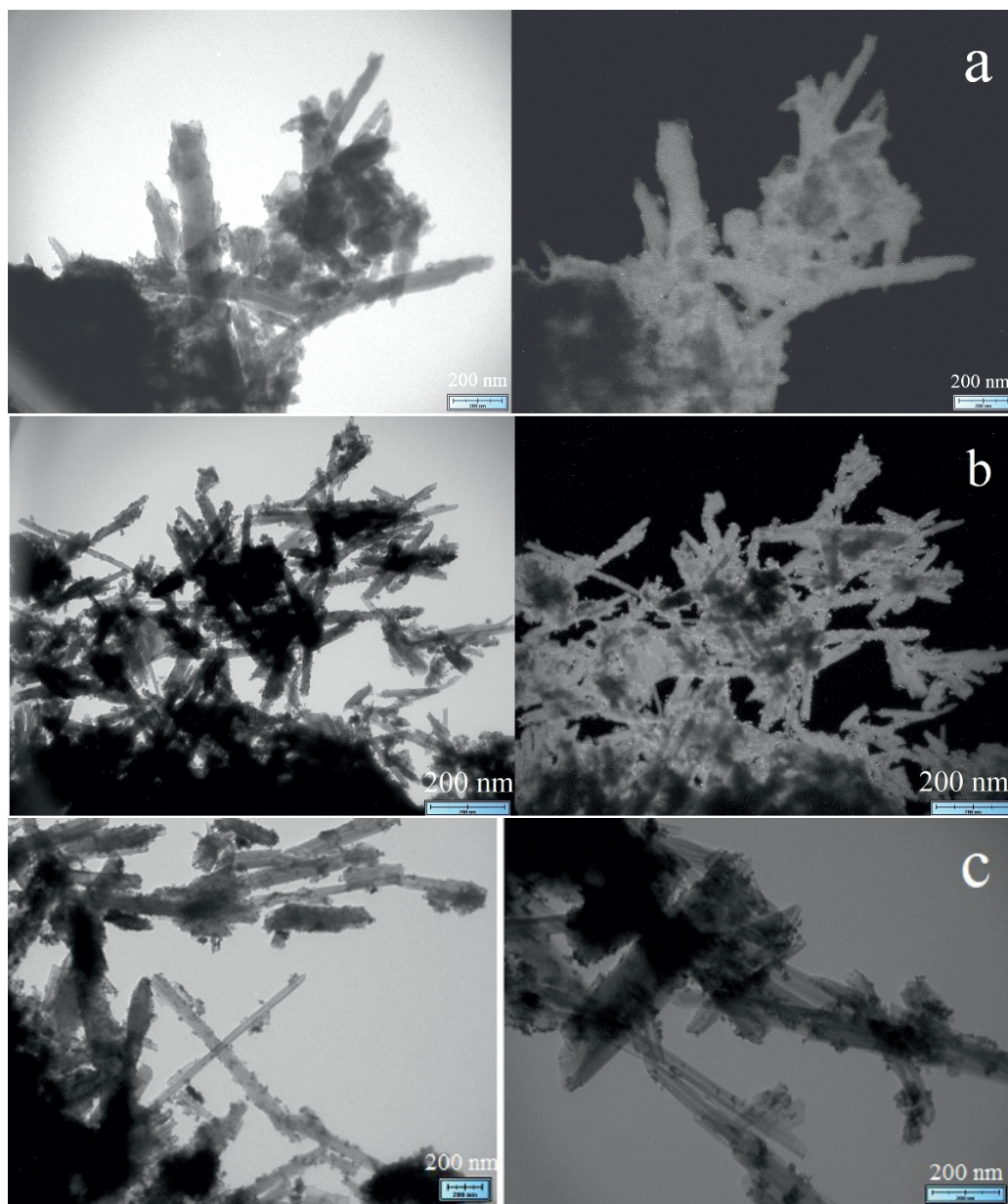


Fig. 2. TEM images in the bright and dark fields of synthesized HNTs@CeO₂ nanocomposites with 3 (a) and 5 wt% (b) the modifier content and HNTs@CeO₂ 5 wt% (c) with 106 magnification

HNTs@CeO₂ nanocomposite (5 wt%) it was observed that some minor aggregation of the CeO₂ nanoparticles had occurred. They formed agglomerates consisting of approximately 4–8 particles (Fig. 2c). Detailed analysis of TEM images of the HNTs part, did not indicate that cerium was present in their cavities.

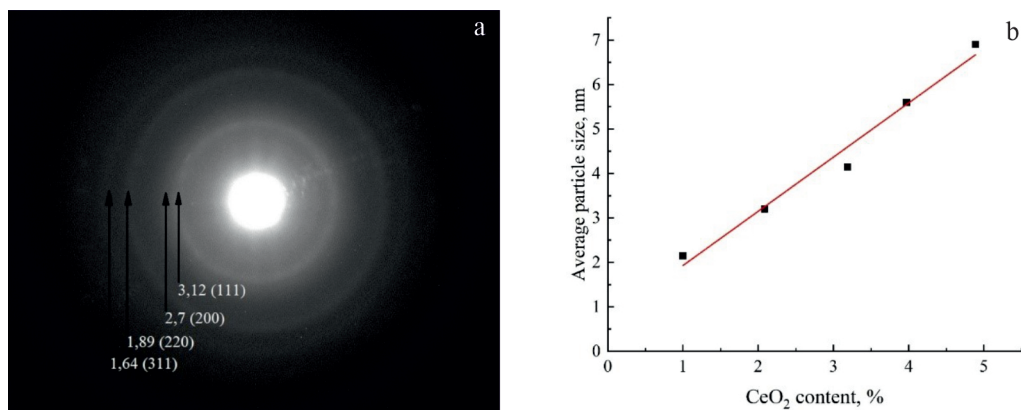


Fig. 3. Research of nanocomposites: a – Electron diffraction pattern of the CeO₂ based modifier of the halloysite nanotubes; b – Dependence of the average particle size of cerium oxide on its content in nanocomposites

Electron diffraction studies of particles with reflections d -values and (hkl) of 3.12 (111), 2.7 (200), 1.89 (220), and 1.64 Å (311) indicate that they belong to the CeO₂ (Fig. 3a). The values of (220) and (311) reflexes are higher by 0.01 Å compared to those typical for CeO₂ bulk. The reason may be the poor orderliness of the synthesized nanoparticles [19]. The CeO₂ content (C) was correlated to the particle diameters (D) by a linear function $D = 0.711 + 1.219C$, $R^2 = 0.98$ (Fig. 3b) at modifier concentrations up to 5%. Assuming that the size of the nuclei is largely independent of the CeO₂ concentration, it becomes logical that the particle diameters are larger for HNTs@CeO₂ with high cerium content compared to those with low content, due to crystal growth effects [20]. In our opinion, the nanoscale carrier acts as a nucleation promotor (heterogeneous nucleation), and the small size of the CeO₂ is explained by the significant number of heterogeneous contacts between nanotubes, which contribute to the nucleation of small particles. Hence, it can be presumed that the heterogeneous surface of the HNTs substrate can influence significantly the growth of the CeO₂ due to Van der Waals forces at the nucleation stage but after nucleation it seems that the crystal growth and hence the particle size becomes linearly dependent on the cerium supply/concentration.

Conclusions. In this study, HNTs modified with CeO₂ nanoparticles were synthesized. The synthesis of the HNTs@CeO₂ nanomaterials was carried out in aqueous solution without stabilizers, in line with the principles of “green” chemistry. According to mapping elemental analysis of the samples, cerium was evenly distributed on the carrier surface. The underlying hypothesis in this study was that CeO₂ could be a viable alternative to TiO₂ or ZnO nanoparticles as inorganic UV filters. CeO₂ has a comparably low photocatalytic activity and high absorption in the UV region. Using a support such as the halloysite clay may reduce the potential of uptake of nanoparticles through the skin.

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